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Anchoring of photochromic spiroxazine into silica xerogels

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Abstract

Synthesis and properties of organically modified silica xerogels for covalent immobilization of photochromic spiroxazine were reported. These xerogels were found to be photochromic in solid state.

Keywords: Photochromism; Silica xerogel; Spiroxazine; First-order kinetics

1. Introduction

Materials composed of both inorganic and organic entities are called hybrid materials. The sol–gel process is particularly well suited to create inorganic–organic hybrid materials, because the solids are formed at low temperatures, at which organic groups are not degraded. The gel materials are referred to as aquagel when water is used as the primary solvent and alcogel when alcohol is used instead. Aero- and xerogels are prepared by sol–gel processing [1]. The difference between the two types of materials lies in the method of drying after sol–gel processing. The encapsulated liquid can be removed from a gel by either evaporative drying or processing at supercritical conditions. The sol–gel provides a convenient method for the production of organically modified surfaces by incorporating alkoxysilane monomers that contain desirable functional groups in the starting polymerization mixture. Organically modified siloxanes can be tailored from commercially available organofunctional alkoxysilanes. In recent years, photochromic and thermochromic spiropyrans and spiroxazines have been receiving considerable attention, due to their potential application in many new technologies, such as data recording and storage, optical switching, displays, and non-linear optics [2,3]. Although the photochromism of spiropyran has been extensively studied [4,5], little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects. However, the replacement of the benzopyran ring by a naphthoxazine ring results in spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation, which confers a much more commercial importance on them [6].

In this paper, we report on the synthesis and photochromic properties of the photochromic silica xerogels by the formation of a covalent link between spiroxazine and preformed sol–gel precursor.

2. Experimental

2.1. Characterization

Melting points were determined using an Electrothermal IA900 and are uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 Analyzer. Mass spectra were recorded using a Shimadzu QP-1000 spectrometer with electron

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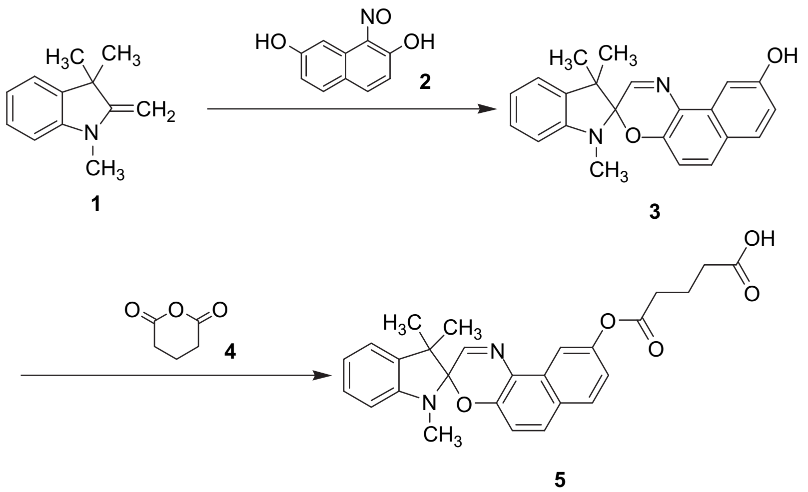


Scheme 1.

energy 70 eV and direct sample introduction. ^{1}H NMR spectra were recorded on Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. A multichannel photodiode detector (MCPD, Otsuka Electronics) was used to obtain visible absorption spectra of organically modified silica xerogels. The specific surface area was determined by the NOVA 2000, Version 7.02 (BET) method at 77.4 K in the partial pressure range $0.1 < p/p_0 < 0.3$. The total pore volume was obtained from the N_2 desorption isotherm.

2.2. Intermediate **3**

Compound **3** was prepared from 1,3,3-trimethyl-2-methyleneindoline **1** and 1-nitroso-2,7-dihydroxy naphthalene **2** according to the method described in Ref. [7]. Yield 3.23 g (23.5%), m.p. 211–214 °C. ^{1}H NMR ($CDCl_3$): δ 7.76 (2H, m), 7.67 (1H, d, $J = 8.8$ Hz), 7.62 (1H, d, $J = 8.8$ Hz), 7.19 (1H, m), 7.12 (1H, $J = 7.3$ Hz), 6.99 (1H, m), 6.92 (1H, m), 6.77 (1H, d, $J = 8.8$ Hz), 6.62 (1H, d, $J = 7.8$ Hz), 2.72 (3H,s), 1.29 (6H, m). Elemental analysis: C, 76.02; H, 5.93; N, 8.10. $C_{22}H_{20}N_2O_2$ requires: C, 76.72; H, 5.85; N; 8.13.

2.3. Spiroxazine **5**

Compound **3** (2.4 g, 6.98 mmol), glutaric anhydride **4** (0.8 g, 7.01 mmol) in benzene (100 ml) was refluxed for 36 h. The precipitated solid was filtered and dried. Recrystallization from *n*-hexane afford 0.73 g (22.7%) of the spiroxazine **5**. M.p. 188–191 °C, ^{1}H NMR ($CDCl_3$): δ 8.22 (1H, d, $J = 2.2$ Hz), 7.75 (1H, d, $J = 8.8$ Hz), 7.22 (1H, s), 7.65 (1H, d, $J = 8.9$ Hz), 7.22 (1H, d, $J = 8.9$ Hz), 7.13 (2H, m), 6.98 (1H, d, $J = 8.8$ Hz), 6.90 (1H, m), 6.58 (1H, d, $J = 4.8$ Hz), 2.76 (5H, m), 2.58 (2H, t, $J = 7.2$ Hz), 2.14 (2H, m), 1.35 (3H,s), 1.34 (3H, s). Elemental analysis: C, 70.39; H, 5.80; N, 5.92. $C_{27}H_{26}N_2O_5$ requires: C, 70.73; H, 5.72; N, 6.11 (Scheme 1).

2.4. Sol–gel processing of $(EtO)_3Si(CH_2)_3NH_2/Si(OEt)_4$ mixtures and covalent immobilization of spiroxazine **5**

Organically modified silica xerogels (**OMSX**) were prepared by sol–gel method of a mixture of tetraethoxysilane $Si(OEt)_4$, 3-aminopropyl-triethoxysilane $(EtO)_3Si(CH_2)_3NH_2$, water and methanol in different ratio followed by air drying (Table 1).

The physical data of the xerogels are given by in Table 2. A stirred solution of **OMSX** (0.1 g), spiroxazine **5** (0.275 g, 0.6 mmol) in methanol (100 ml) containing *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide (EDC) (1.15 g, 6 mmol) was refluxed for 24 h. The mixture was then washed repeatedly with methanol to remove the last trace of the unreacted spiroxazine and air dried (Scheme 2).

3. Results and discussion

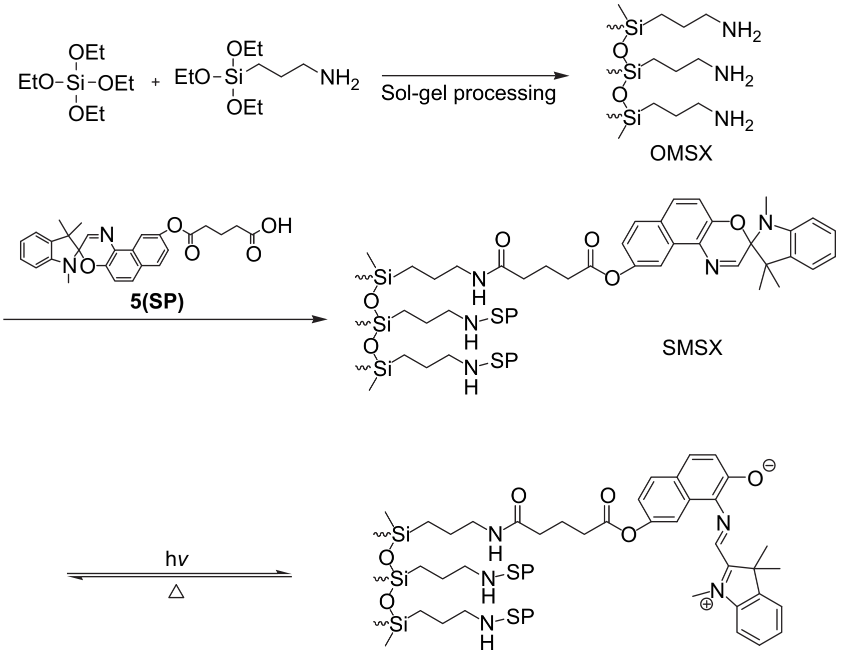
The synthetic route to the spiroxazine **5** is outlined in Scheme 1. The reaction of 1,3,3-trimethyl-2-methyleneindoline **1**

Table 1
Preparation of the wet gels

Sample	Precursors (g [mmol])				Gel time (h)
	$Si(OEt)_4$	$(EtO)_3Si(CH_2)_3NH_2$	MeOH	H_2O	
OMSX-10	12.52 (60.084)	1.48 (6.676)	100	5.4	24
OMSX-20	11.13 (53.408)	2.96 (13.352)	100	5.4	24
OMSX-30	9.74 (46.732)	4.43 (20.028)	100	5.4	24

Table 2
Structural characteristics of the xerogels

	Specific surface area (m^2/g)	Average pore radius (Å)
OMSX-10	94	32
OMSX-20	109	33
OMSX-30	107	50



Scheme 2.

with nitrosodihydroxynaphthalene **2** gave the compound **3** in 23.5% yield. The reaction of compound **3** with glutaric anhydride **4** gave spiroxazine **5** in 22.7% yield. Silica xerogels modified by amino-substituted organic groups were prepared by sol–gel processing of $(EtO)_3Si(CH_2)_3NH_2/Si(OEt)_4$ mixtures, followed by air drying of the wet gels. The amino groups accessible for the reaction with spiroxazine were then determined by acid–base titration. **OMSX-10**, **OMSX-20** and **OMSX-30** contain 6, 26 and 44 mmol of amino groups per gram, respectively. Particle size increased as the number of amino groups increased: 59.4 nm in **OMSX-10**, 67.32 nm in **OMSX-20**, 87.2 nm in **OMSX-30**. Spiroxazine **5** was immobilized on **OMSX** prepared by using $(EtO)_3Si(CH_2)_3NH_2$ and $Si(OEt)_4$ using a small amount of EDC. Spiroxazine modified silica xerogel (**SMSX**) was dried at room temperature to constant weight.

The photochromic reaction is caused by the reversible heterolytic cleavage of the C(spiro)–O bond under UV irradiation, yielding the coloured form that can return to the colourless form by ring closure under visible light irradiation or in the dark. Irradiation of **SMSX**s was carried out using an ultra-thin pressed pellet. Electronic absorption spectral changes of **SMSX** upon UV irradiation are depicted in Fig. 1. Upon UV irradiation, a broad absorption band appeared at around 605 nm which increased with increasing irradiation time. When the sample was left in the dark at room temperature after irradiation, the absorbance at 605 nm decreased rapidly.

The original spectral pattern is reversibly recovered within 15 s. The new band is ascribed to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiation are at any time proportional to each other in the visible region, indicating that only one species is formed. This allowed the absorption to be monitored at a λ_{max} (605 nm) as a function of time to obtain thermal colour fading rate (k). Tomioka has examined the thermal decolouration rate for photochromic spiropyran derivatives using first-order kinetics [8]. The kinetic equation approach to the open merocyanine to closed spiro form via first-order reaction in the present case is given by

$$\ln(A_t - A_\infty)/(A_i - A_\infty) = kt \qquad (1)$$

where A_i is the absorbance at 605 nm, and A_t is the absorbance at 605 nm at time t after UV irradiation. A_∞ and k refer to absorbance at 605 nm after 1 h and first-order colour changing rate constant, respectively. In the thermal colour changing

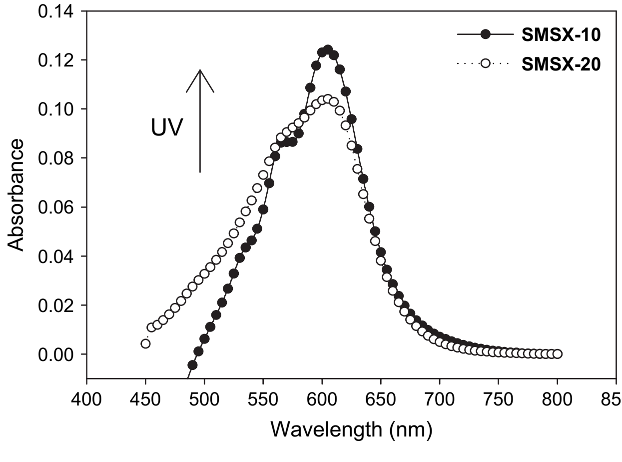


Fig. 1. Visible spectral changes of **SMSX**s upon UV irradiation.

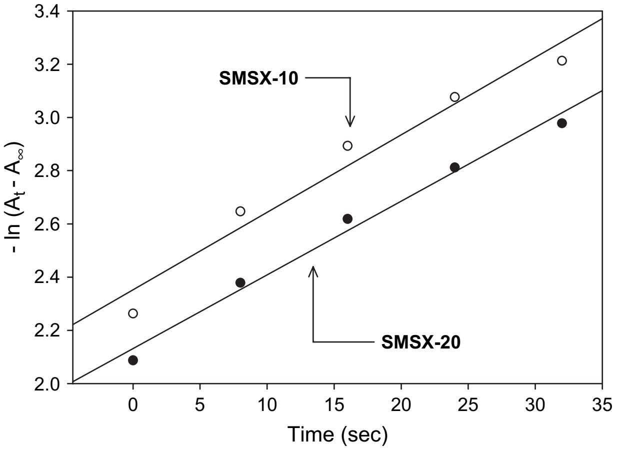


Fig. 2. First-order decolouration kinetic plot of photoisomerization (merocyanine → spiro) reaction of **SMSX**: (a) **SMSX-10** (b) **SMSX-20**, respectively.

process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the decolouration rate constant, k. First-order plots according to Eq. (1) for **SMSX-10** and **SMSX-20** are shown in Fig. 2. The first-order decolouration constants of **SMSX-10** and **SMSX-20** were 2.78×10^{-2} and 2.91×10^{-2}, respectively.

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